3122 *Inorg. Chem.* **1998,** *37,* 3122−3126

Reactions of the Dirhenium(II) Complexes Re_2X_4(*μ*-dppm)$_2$ (X = Cl, Br; dppm = $Ph_2PCH_2PPh_2$) with Isocyanides. 16.[1] Complexes of the Type [Re_2(*μ*-Br)$_2$(*μ*-dppm)$_2$Br(CO)(CNXyl)$_2$]Y (Y = O_3SCF_3, PF_6) That Exist in Isomeric Forms with Boat and Chair Conformations for the [Re_2(*μ*-dppm)$_2$] Unit

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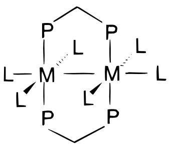
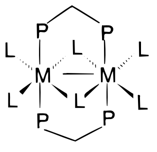
Introduction

The reactions of the dirhenium(II) synthons Re_2X_4(*μ*-dppm)$_2$ (X = Cl, Br; dppm = $Ph_2PCH_2PPh_2$) with various combinations of CO and organic isocyanide ligands have led to several series of bioctahedral complexes which have structures based upon open bioctahedral (**A**) and edge-sharing bioctahedral (**B**) geometries. In some instances, structural isomers have been isolated, the most striking instances being in the case of the salts of the [Re_2X_3(*μ*-dppm)$_2$(CO)(CNXyl)$_2$]$^+$ cations (Xyl = 2,6-dimethylphenyl), which have been identified in at least six different structural forms (Chart 1).[1−7] The identity of all but one of these (structure **6**) have been confirmed by single-crystal X-ray structure determinations. During the course of our studies on the synthesis and characterization of the dirhenium cation **5** (X = Br), which we isolated as its $O_3SCF_3^-$ and PF_6^- salts,[6] we obtained spectroscopic evidence for the existence of this complex in two very similar structural forms. One of these was characterized by X-ray crystallography;[6] the other was not. Further studies of **5** have now established that preparative samples of its $O_3SCF_3^-$ and PF_6^- salts consist of a mixture of two isomers with the same basic structure as that depicted in Chart 1, but which differ in possessing either a boat or a chair conformation for the Re_2(*μ*-dppm)$_2$ unit. As far as we are aware, this system constitutes the first in which isomers with boat and chair conformations for an M_2(*μ*-dppm)$_2$ unit have been structurally characterized.[8]

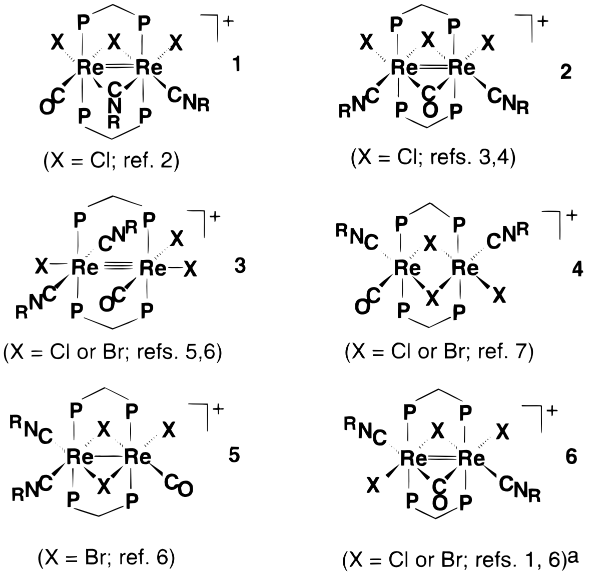


A



B

Chart 1. Isomers of [Re_2X_3(*μ*-dppm)$_2$(CO)(CNR)$_2$]$^+$ Cations (X = Cl, Br; R = Xyl) **1**−**6**[a]



(X = Cl; ref. 2)

(X = Cl; refs. 3,4)

(X = Cl or Br; refs. 5,6)

(X = Cl or Br; ref. 7)

(X = Br; ref. 6)

(X = Cl or Br; refs. 1, 6)a

[a] This is the most likely structure based upon its spectroscopic properties and chemical reactivity.

Experimental Section

Starting Materials and General Procedures. The complexes [Re_2(*μ*-Br)$_2$(*μ*-dppm)$_2$Br(CO)(CNXyl)$_2$]Y (Y = O_3SCF_3, **5a** (chair)/**5a′**(boat); Y = PF_6, **5b**(chair)/**5b′**(boat)) were prepared by the previously described literature procedures, with the use of Re_2Br_4(*μ*-dppm)$_2$(CO)(CNXyl) and [Re_2Br_3(*μ*-dppm)$_2$(CO)(CNXyl)]Y as starting materials.[6] The compound [(η^5-C_5H_5)$_2$Fe]PF_6 was prepared by the literature method,[9] while (η^5-C_5H_5)$_2$Co was purchased from the Aldrich Chemical Co. Solvents were obtained from commercial sources and were deoxygenated by purging with dinitrogen prior to use. All reactions were performed under an atmosphere of dry dinitrogen. Infrared spectra, ^{1}H and ^{31}P{^{1}H} NMR spectra, and cyclic voltammetric measurements were determined as described previously.[10] Elemental microanalyses were carried out by Dr. H. D. Lee of the Purdue University Microanalytical Laboratory.

A. Synthesis of Re_2(*μ*-Br)$_2$(*μ*-dppm)$_2$Br(CO)(CNXyl)$_2$, 7. A sample of **5a** (120 mg, 0.0659 mmol) was treated with (η^5-C_5H_5)$_2$Co (12.5 mg, 0.0661 mmol) in 15 mL of dichloromethane at 25 °C. A color change of the solution from red-brown to green was observed within 5 min of mixing. The resulting solution was stirred for a total of 30 min to ensure the completion of the reaction. The reaction mixture was then filtered to remove any insoluble material, and the volume of the green filtrate was reduced to ∼2 mL. An equal volume of diethyl ether (∼2 mL) was added to induce precipitation of [(η^5-C_5H_5)$_2$Co]O_3SCF_3. This pale yellow byproduct was filtered off and the filtrate evaporated under a stream of dinitrogen. The

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title complex **7** was collected as a green solid, washed with diethyl ether (3 × 5 mL), and dried under vacuum. Yield, 94 mg (85%). Anal. Calcd for $C_{69}H_{62}Br_3N_2OP_4Re_2$: C, 49.59; H, 3.73; N, 1.68. Found: C, 49.21; H, 3.65; N, 1.48. IR (ν, cm^{-1}): 2050 (sh), 2012 (s), 1919 (s, br), 1858 (vs). The cyclic voltammogram of a solution of **7** in 0.1 M n-Bu_4NPF_6−CH_2Cl_2 was identical to that of **5**.[6]

B. Oxidation of 7 to 5b. A sample of **7** (42.0 mg, 0.0251 mmol) in 10 mL of dichloromethane was treated with 9.0 mg of $[(\eta^5\text{-}C_5H_5)_2Fe]PF_6$ (0.027 mmol) and the mixture stirred at 25 °C for 1 h. The reaction mixture was reduced in volume to ~1 mL, and 15 mL of diethyl ether was added slowly with stirring to induce precipitation of the red-brown product **5b**, which was filtered off, washed with diethyl ether (3 × 5 mL), and dried under vacuum. Yield, 41.5 mg (91%). The identity of this product was based on a comparison of its spectroscopic properties with those of an authentic sample.[6]

C. Conversion of 5b′ (Boat Conformer) to 5b (Chair Conformer). A solution of **5b′** (20.0 mg) in 5 mL of dichloromethane was stirred at room temperature for 96 h. The solvent was evaporated under a stream of dinitrogen and the residue of **5b** washed with diethyl ether (3 × 3 mL) and dried under vacuum. Yield, 18.5 mg (93%). The identity and purity of **5b** was established by IR and NMR spectroscopy.[6]

A similar conversion of **5b′** to **5b** was carried out in refluxing dichloromethane with a reaction time of 24 h. The spectroscopic properties of this product indicated that, like the room-temperature reaction, the conversion of **5b′** to **5b** was essentially complete.

D. Attempted Conversion of 5b to 5b′. A sample of **5b** (100 mg) was dissolved in 30 mL of CH_2Cl_2, and the resulting solution was stirred at 25 °C for 24 h. The solvent was removed by the use of a rotary evaporator, and the residue was washed with diethyl ether (3 × 5 mL) and dried under vacuum. It was shown to be unreacted **5b**. When this sample was redissolved in dichloromethane and the solution refluxed for 24 h, unreacted **5b** could again be recovered quantitatively. A similar observation was made when 1,2-dichloroethane was used as the solvent.

X-ray Crystallography. Single crystals of **5b** and **7** were grown at 25 °C from solutions in CH_2Cl_2/i-Pr_2O and CH_2Cl_2/$CH_3CH_2C(O)OCH_3$, respectively, by slow evaporation of the solvents. The data collections were performed on an Enraf-Nonius CAD4 computer-controlled diffractometer with graphite-monochromatized Mo Kα radiation at 203 ± 1 K. The cell constants were based on 25 reflections obtained randomly in the range of $11 < \theta < 21°$ for **5b** and $19 < \theta < 25°$ for **7**, as measured by the computer-controlled diagonal slit method of centering. Three standard reflections were measured after every 5000 s of beam time during the data collection to monitor the stability of the crystals. The intensities of these standard reflections remained constant within experimental error throughout the data collections. Calculations were performed on an AlphaServer 2100 computer by use of the Enraf-Nonius structure determination package (MolEN)[11] for structure solving and SHELXL-93[12] for refinements. Lorentz and polarization corrections were applied to the data sets. An empirical absorption correction was also applied,[13] but no corrections for extinction were made.

Both compounds **5b** and **7** crystallized in a triclinic crystal system. The space group $P\bar{1}$ was assumed for both and was confirmed by the successful solutions and refinements of the structures. Hydrogen atoms in both structures were calculated using idealized geometries with C−H = 0.95 Å and $U = 1.3U_{eq}(C)$. Their contributions were added to the structure factor calculations, but their positions were not refined. Corrections for anomalous scattering were applied to all refined atoms in both structures.[14]

The structure of **5b** was solved by a combination of direct methods (DIRDIF 92)[15] and difference Fourier analyses. During the course of the structure analysis, a disorder between the terminal CO and Br ligands associated with Re(1) was found. This disorder is about a pseudo-2-fold axis along the Re−Re bond axis. A 50/50% disorder model was refined satisfactorily for this structure. Two molecules of CH_2Cl_2 from the crystallization solvent were found cocrystallized with **5b** in the asymmetric unit. They were included in the analysis and refined satisfactorily. Two carbon atoms, C(10) and C(125) and the atoms of the disordered CO ligand were refined isotropically. The remaining non-hydrogen atoms were refined with anisotropic thermal parameters. The structure was refined in full-matrix least squares where the function minimized was $\sum w(|F_o|^2 - |F_c|^2)^2$. The weighting factor w is defined as $w = 1/[\sigma^2(F_o^2) + (0.1596P)^2 + 26.4359P)$, where $P = (F_o^2 + 2F_c^2)/3$. The final residuals for **5b** were $R = 0.065$ and $R_w = 0.185$ with GOF = 1.021. The two highest peaks in the final difference Fourier map were 4.27 and 3.93 e/Å^3. They were located at distances in the range 1.26−1.81 Å from the Re atoms and 2.00−2.27 Å from the bridging Br atoms. These features may have their origin in the presence of an additional minor disorder in the structure which we were not able to model satisfactorily. Nonetheless, these undesirable aspects of the structure determination do not in any significant way affect the key structural results and conclusions.

The structure of **7** was also solved by a combination of direct method (DIRDIF92)[15] and difference Fourier analyses. As with the structure of **5b**, there is also a disorder between the terminal CO and the Br ligands (about Re(2)), but in this case, a disorder model involving *fractional* CO and Br occupancies for each site was refined satisfactorily to 0.707(6) CO/0.293(6) Br for one site and 0.293(6) CO/0.707(6) Br for the other. All non-hydrogen atoms except for those of the minor component of the disordered CO ligand, C(2) and O(2), were refined anisotropically; C(2) and O(2) were refined with isotropic thermal parameters. During the final stage of this analysis, a CH_2Cl_2 solvent molecule from the crystallization solvent was found to be cocrystallized with **7** in the asymmetric unit. Atoms of this solvent molecule were located from the difference Fourier analyses and satisfactorily refined with anisotropic thermal parameters. A badly disordered ethyl acetate molecule of uncertain multiplicity was also found in the asymmetric unit. This solvent molecule was included in the refinement by using the SQUEEZE technique.[16] The structure was refined in full-matrix least squares where the function minimized was $\sum w(|F_o|^2 - |F_c|^2)^2$ and the weighting factor w is defined as $w = 1/[\sigma^2(F_o^2) + (0.0768P)^2 + 4.1358P]$, where $P = (F_o^2 + 2F_c^2)/3$. The final residuals for **7** were $R = 0.040$ and $R_w = 0.112$ with GOF = 1.099. The largest remaining peak in the final difference Fourier map was 1.14 e/Å^3.

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Table 1. Crystallographic Data for the Dirhenium Complexes $[Re_2(\mu\text{-}Br)_2(\mu\text{-}dppm)_2Br(CO)(CNXyl)_2]PF_6\cdot 2CH_2Cl_2$, **5b**, and $Re_2(\mu\text{-}Br)_2(\mu\text{-}dppm)_2Br(CO)(CNXyl)_2\cdot CH_2Cl_2$, **7**

	5b	7
empirical formula	$Re_2Br_3Cl_4P_5F_6ON_2C_{71}H_{66}$	$Re_2Br_3Cl_2P_4ON_2C_{70}H_{64}$
fw	1986.13	1756.23
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a, Å	13.800(5)	13.330(4)
b, Å	16.927(8)	16.226(3)
c, Å	17.556(5)	16.327(6)
α, deg	87.05(7)	99.29(2)
β, deg	77.56(6)	90.66(3)
γ, deg	69.67(7)	91.59(2)
V, Å^3	3753(7)	3483(3)
Z	2	2
ρ_{calcd}, g/cm^3	1.757	1.674
μ, mm^{-1}	5.153	5.434
radiation (λ, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
trans factors, min/max	0.54/0.91	0.64/0.88
temp, K	203	203
$R(F_o)$	0.065	0.040
$R_w(F_o^2)$	0.185	0.112
GOF	1.021	1.099

Table 2. Comparison of Selected Bond Distances and Bond Angles for $[Re_2(\mu\text{-}Br)_2(\mu\text{-}dppm)_2Br(CO)(CNXyl)_2]PF_6\cdot 2CH_2Cl_2$, **5b**, and $Re_2(\mu\text{-}Br)_2(\mu\text{-}dppm)_2Br(CO)(CNXyl)_2\cdot CH_2Cl_2$, **7**[a]

5b		**7**	
	Distances (Å)		
Re(1)−Re(2)	3.028(2)	Re(1)···Re(2)	3.8023(10)
Re(2)−Br(3B)	2.562(6)	Re(1)−Br(1)	2.509(2)
Re(2)−Br(1)	2.556(2)	Re(1)−Br(2)	2.6184(11)
Re(2)−Br(2)	2.553(3)	Re(1)−Br(3)	2.5813(9)
Re(2)−C(3A)	1.89(4)	Re(1)−C(1)	1.838(14)
Re(2)−P(2)	2.452(5)	Re(1)−P(1)	2.444(2)
Re(2)−P(4)	2.439(5)	Re(1)−P(3)	2.451(2)
Re(1)−Br(1)	2.599(3)	Re(2)−Br(2)	2.6289(9)
Re(1)−Br(2)	2.604(3)	Re(2)−Br(3)	2.6560(11)
Re(1)−C(20)	2.00(2)	Re(2)−C(10)	1.929(7)
Re(1)−C(10)	2.02(2)	Re(2)−C(20)	1.931(7)
Re(1)−P(1)	2.438(5)	Re(2)−P(2)	2.407(2)
Re(1)−P(3)	2.437(5)	Re(2)−P(4)	2.387(2)
	Angles (deg)		
P(2)−Re(2)−P(4)	178.75(4)	P(1)−Re(1)−P(3)	166.02(5)
C(3A)−Re(2)−Br(3B)	78.6(10)	C(1)−Re(1)−Br(1)	91.9(4)
C(3A)−Re(2)−Br(2)	84.5(10)	C(1)−Re(1)−Br(3)	97.7(4)
Br(3B)−Re(2)−Br(1)	88.9(2)	Br(1)−Re(1)−Br(2)	82.81(4)
Br(2)−Re(2)−Br(1)	109.50(9)	Br(3)−Re(1)−Br(2)	87.75(3)
P(1)−Re(1)−P(3)	178.78(14)	P(2)−Re(2)−P(4)	168.58(5)
C(20)−Re(1)−C(10)	89.2(7)	C(10)−Re(2)−C(20)	90.1(3)
C(10)−Re(1)−Br(1)	82.1(5)	C(20)−Re(2)−Br(2)	94.7(2)
C(20)−Re(1)−Br(2)	82.3(5)	C(10)−Re(2)−Br(3)	89.1(2)
Br(1)−Re(1)−Br(2)	106.58(9)	Br(2)−Re(2)−Br(3)	85.99(3)
Re(2)−Br(1)−Re(1)	71.95(9)	Re(1)−Br(2)−Re(2)	92.87(3)
Re(2)−Br(2)−Re(1)	71.91(9)	Re(1)−Br(3)−Re(2)	93.09(3)
O(3A)−C(3A)−Re(2)	165(4)	O(1)−C(1)−Re(1)	178.6(13)
N(20)−C(20)−Re(1)	176.6(14)	N(10)−C(10)−Re(2)	179.0(6)
N(10)−C(10)−Re(1)	176.0(15)	N(20)−C(20)−Re(2)	174.7(7)

[a] Comparisons are made between corresponding parameters in the two structures as represented by the labeling schemes in Figures 2 and 3. Numbers in parentheses are estimated standard deviations in the least significant digits.

The crystallographic data for **5b** and **7** are given in Table 1, while important intramolecular bond lengths and angles for **5b** and **7** are given in Table 2.

Results and Discussion

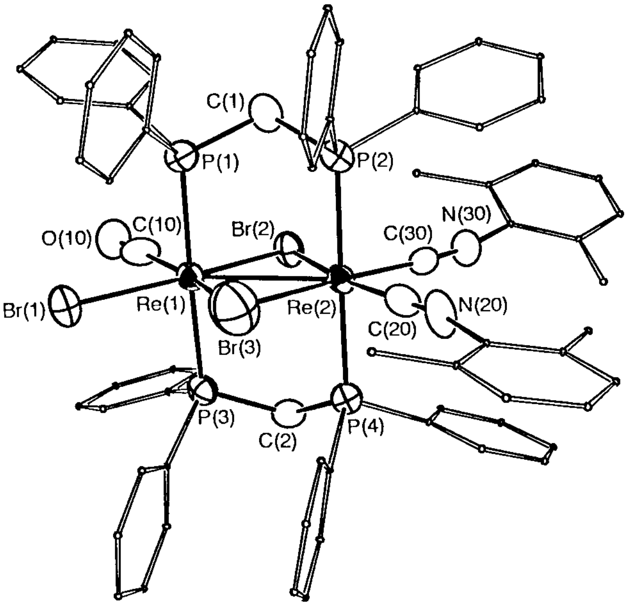

Figure 1. Structure of the isomeric form of the $[Re_2(\mu\text{-}Br)_2(\mu\text{-}dppm)_2Br(CO)(CNXyl)_2]^+$ cation in which the $[Re_2(\mu\text{-}dppm)_2]$ unit has a boat conformation (taken from ref 6).

An earlier study[6] of di-μ-bromo-bridged dirhenium complexes of the type $[Re_2(\mu\text{-}Br)_2(\mu\text{-}dppm)_2Br(CO)(CNXyl)_2]Y$ (Y = O_3SCF_3, PF_6) had been complicated by the realization that they occur as mixtures of two species (isomers?) possessing very similar spectroscopic properties and essentially identical electrochemical properties. While this behavior was independent of the anion ($O_3SCF_3^-$ or PF_6^-), the ratio of components of these mixtures depended on the synthetic strategy that was used.[6] In our previous report,[6] we described the successful separation and structural characterization of one of the components of the mixture, i.e., that of the di-μ-bromo bridge complex shown in Figure 1, which contains a weak Re−Re single bond and a boat (tub) conformation for the $PCH_2PReRePCH_2P$ unit. From a combination of chemical reactivity studies and the further use of X−ray crystallography, we have now identified the other component in these mixtures to be the isomer in which the $[Re_2(\mu\text{-}dppm)_2]$ unit possesses a chair, rather than boat, conformation. In subsequent discussions of $[Re_2(\mu\text{-}Br)_2(\mu\text{-}dppm)_2Br(CO)(CNXyl)_2]Y$, the chair and boat isomers will be labeled **5** and **5′**, respectively, while **a** and **b** will signify the triflate and hexafluorophosphate salts, respectively.[17]

In the case of **5a** and **5b**, whose structures were not originally determined,[6] we have now been able to obtain the pure triflate salt **5a** in sufficient quantities to enable us to convert it to its neutral reduced congener $Re_2(\mu\text{-}Br)_2(\mu\text{-}dppm)_2Br(CO)(CNXyl)_2$, **7**, through the use of cobaltocene as the reducing agent. This reductant accessed the one-electron reduction that is characterized by the couple at $E_{1/2} = +0.11$ V vs Ag/AgCl.[6] The paramagnetic compound **7** showed very broad and poorly defined resonances in its ^1H NMR spectrum (recorded in $CDCl_3$) between $\delta \sim +15$ and $\delta \sim +1$, while a solution in $CDCl_3$ had a magnetic moment of $1.5 \pm 0.2\ \mu_\beta$, as determined by the Evans method.[18] Like its cationic precursor **5a**, the IR spectrum of **7** (recorded as a Nujol mull) showed the presence of terminal XylNC and CO ligands, with ν(CN) at 2050, 2012, and 1919 cm^{-1} and ν(CO) at 1858 cm^{-1}. A comparison of the IR spectra of **5a** and **7** shows the expected shift of the ν(CN) and ν(CO)

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(17) In an earlier report,[6] we used the labels **4a** (chair)/**4a′**(boat) for Y = O_3SCF_3 and **4b**(chair)/**4b′**(boat) for Y = PF_6.

(18) Evans, D. F. *J. Chem. Soc.* **1959**, 2003.

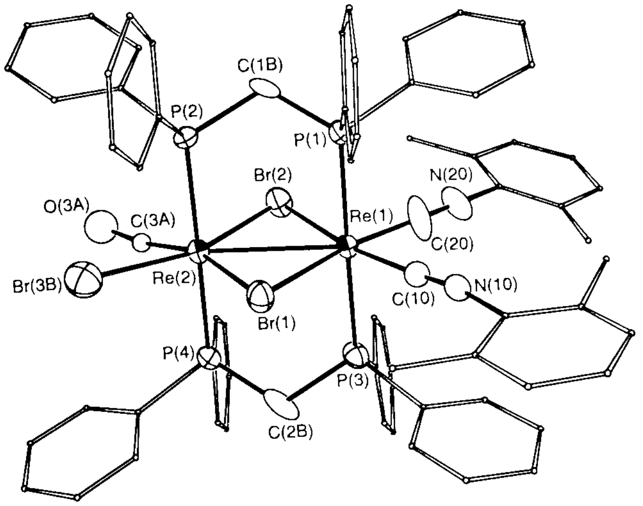


Figure 2. ORTEP[19] representation of the structure of the dirhenium cation $[Re_2(\mu\text{-}Br)_2(\mu\text{-}dppm)_2Br(CO)(CNXyl)_2]^+$ as present in **5b**, showing half the disorder involving the terminal CO and Br ligands. The thermal ellipsoids are drawn at the 50% probability level except for the phenyl group atoms of the dppm ligands and the xylyl group atoms of the XylNC ligand, which are circles of arbitrary radius.

modes to lower frequences as the oxidation state of the dimetal core is reduced, in accord with increased Re to π^*(CNXyl) and π^*(CO) back-bonding in **7**.

The oxidation of **7** to the hexafluorophosphate salt **5b** by the use of $[(\eta^5\text{-}C_5H_5)_2Fe]PF_6$ established the close structural relationship that must exist between **5a**, **5b**, and **7**. This was confirmed by the determination of the structures of **5b** and **7** by X-ray crystallography, which showed that both complexes possess a chair conformation for the $Re_2(\mu\text{-}dppm)_2$ unit. Thus, the aforementioned conversion **5a** → **7** → **5b** proceeds with retention of the chair conformation. ORTEP[19] representations of the structure of the dirhenium cation present in **5b** and the structure of **7** are shown in Figures 2 and 3.

A comparison of the structural parameters of the dirhenium cation present in **5b** (Table 2) with those reported[6] for the corresponding cation in the structure of **5b′** reveals few differences. The Re−Br, Re−P, and Re−C (xylyl isocyanide) distances in these two structures are essentially identical. The Re−Re single bond distances of 3.028(2) Å for **5b** and 3.0456(8) Å for **5b′** are slightly different, presumably as a consequence of the one major difference between these structures, namely, the conformation of the $PCH_2PReRePCH_2P$ fused ring system. The shorter Re−Re distance is associated with the more stable chair conformation isomer (**5b**).

In comparing the structure of **5b** with that of its one-electron-reduced congener **7**, the parameters for the dirhenium species are essentially the same, with the exception of those associated with the $Re_2(\mu\text{-}Br)_2$ unit (Table 2) which are the result of changes in the Re−Re bond order. The Re−Re bond distances in the structures of **5b** and **7** are 3.028(2) and 3.8023(10) Å, respectively. These distances, along with the magnetic properties of **5** (see ref 6) and **7**, are consistent with the presence of Re−Re bonds of order 1 and 0, respectively. Accordingly, the one-electron reduction of **5a** (and **5b**) leads to the neutral complex $(CO)BrRe(\mu\text{-}Br)_2(\mu\text{-}dppm)_2Re(CNXyl)_2$, **7**, which can best be considered formally as a charge separated Re(II)−Re(I) species (17e−18e) rather than one containing a Re−Re bond of order 0.5.

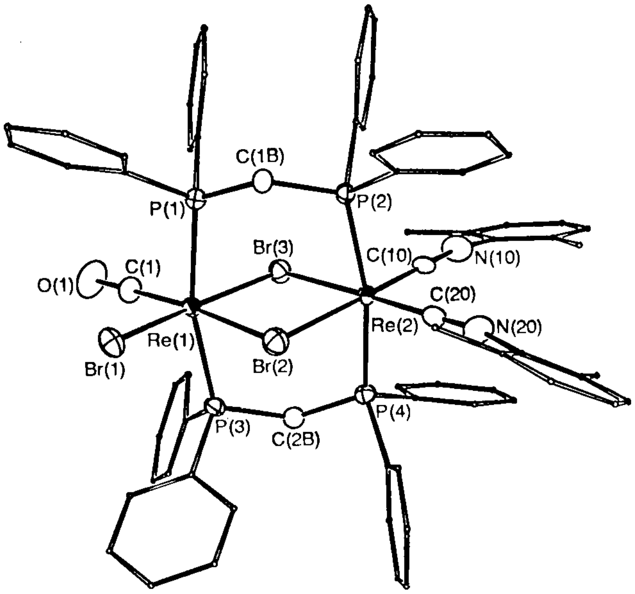
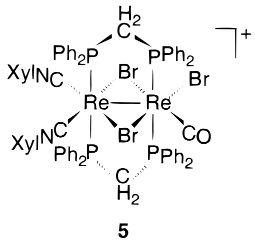


Figure 3. ORTEP[19] representation of the structure of the dirhenium complex $Re_2(\mu\text{-}Br)_2(\mu\text{-}dppm)_2Br(CO)(CNXyl)_2$, **7**, showing half the disorder involving the terminal CO and Br ligands. The thermal ellipsoids are drawn at the 50% probability level except for the phenyl group atoms of the dppm ligands and the xylyl group atoms of the XylNC ligand, which are circles of arbitrary radius.

The large increase in Re−Re distance that accompanies the one-electron reduction of the salts **5a** and **5b** to **7** (~0.8 Å) would be expected to reduce any strain within the $Re_2(\mu\text{-}dppm)_2$ unit and allow conversion to the most stable ring conformation. Since no conformation change occurs, we conclude that the chair conformation, as is already present in **5a** and **5b**, is more stable than the boat conformation in **5a′** and **5b′**. This is supported by the observation that solutions of **5b′** in dichloromethane convert slowly to the more thermodynamically stable isomer **5b** (96 h at 22 °C, 24 h at reflux) in essentially quantitative yield.

Concluding Remarks

The synthesis, separation, and structural characterization of the isomers **5** and **5′**, which differ only in the conformation of the $Re_2(\mu\text{-}dppm)_2$ unit (chair and boat, respectively), provide the first such case in the field of dimetal chemistry with this type of bridging ligand.[20−22] Based upon our current knowledge of the structural chemistry of isomers of the $[Re_2X_3(\mu\text{-}dppm)_2(CO)(CNXyl)_2]^+$ cations (as summarized in Chart 1), it is clear that this type of isomerization is encountered in species in which the two sides of the molecule are very similar (as in **5**) so that one conformer is not favored strongly over the other on the



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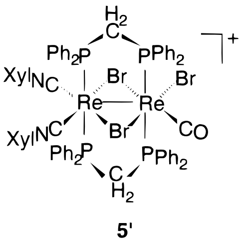

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basis of steric factors. In the case of all other isomers that have so far been structurally characterized (**1**−**4**), only the boat conformer has been identified. In the case of the symmetrical edge-sharing bioctahedral complex $Re_2(\mu\text{-}Cl)_2(\mu\text{-}dppm)_2Cl_4$, the expected chair conformation for the $Re_2(\mu\text{-}dppm)_2$ is indeed found to be present.[23]

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Supporting Information Available: Tables giving details for the crystal data and data collection parameters, atomic positional parameters, anisotropic thermal parameters, bond distances, bond angles and torsion angles for **5b** and **7** (42 pages). Ordering information is given on any current masthead page.

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